

## PATENT ABSTRACTS OF JAPAN

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(54) ELECTROPHOTOGRAPHIC TONER

(57)Abstract:

PURPOSE: To provide the toner which can deal with a high-speed machine, has a high resolution and high image quality and has an excellent pulverization property by using the specific resin produced by a soln. polymn. method and a compd. having a glycidyl group and crosslinking such resin and compd. at a specific ratio.

CONSTITUTION: The binder of the electrophotographic toner consisting of at least coloring agents, binder and charge control agent, is constituted of a COOH- contg. vinyl resin (A) having 1,000 to 20,000 number-average mol.wt. (Mn) and 5.0 to 100 acid value and 40 to 75° C Tg point and the glycidyl compd. (B) having 0.05 to 1.0equiv. as the glycidyl groups per lequiv. of the COOH groups in the COOH-contg. vinyl resin (A). The compsn. formed by using this COOH- contg. vinyl resin (A) and this glycidyl compd. (B) is melted and kneaded and the kneaded matter obtd. in such a manner is pulverized. The process for production of the COOH-contg. vinyl resin (A) is preferably soln. polymn.

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CLAIMS

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## [Claim(s)]

[Claim 1] the toner for electrophotography which consists of a coloring agent, a binder, and an electric charge regulator at least — setting — this binder — (number-average-molecular-weight Mn) 1,000 —20,000 and the acid number 5.0—100 it is — and per 1Eq of COOH radicals in the COOH content vinyl resin (A) whose Tg point is 40—75 degrees C, and this COOH content vinyl resin (A) — as a glycidyl group — 0.05—1.0 Toner for electrophotography characterized by consisting of glycidyl compounds (B) which have the equivalent.

[Claim 2] The toner for electrophotography according to claim 1 this whose binder is the resin constituent to which COOH content vinyl resin (A) and a glycidyl compound (B) were made to react.

[Claim 3] The toner for electrophotography according to claim 1 with which COOH content vinyl resin (A) was chosen from the monoester of an acrylic acid, a methacrylic acid, a maleic anhydride, a maleic acid, boletic acid, a cinnamon acid, and a partial saturation dibasic acid and which is obtained by copolymerizing a kind at least.

[Claim 4] The toner for electrophotography according to claim 1 obtained by COOH content vinyl resin (A) copolymerizing at least a kind of vinyl monomer chosen from styrene, acrylic ester, methacrylic acid ester, boletic acid dialkyl ester, acrylonitrile, acrylamide, and methacrylamide.

[Claim 5] The toner for electrophotography according to claim 1 which is glycidyl ester content resin a glycidyl compound (B) is weight average molecular weight 3,000—10,000, and are [ resin ] epoxy value 0.01—0.3Eq / 100g.

[Claim 6] The toner for electrophotography according to claim 1 with which COOH content vinyl resin (B) is manufactured by the solution polymerization method.

[Claim 7] The manufacturing method of the toner for electrophotography to which this binder carries out crosslinking reaction of COOH content vinyl resin (A) and the glycidyl compound (B) in the toner for electrophotography which carried out melting kneading of a coloring agent, a binder, and the electric charge regulator at least, pulverized the obtained kneading object, and was obtained at the time of the above-mentioned melting kneading.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the toner for electrophotography for developing an electrostatic-charge image in electrophotography, electrostatic recording, electrostatic printing, etc. It can respond to a high-speed machine in more detail, and is related with the toner for electrophotography which are moreover high resolution and high definition, and was excellent in the grindability.

[0002]

[Description of the Prior Art] Generally, after the electrophotography direction for use in a PPC copying machine or a printer forming the static electricity-latent image on an optical photo conductor, developing this latent image using a toner subsequently and imprinting a toner image on established sheets, such as paper, the approach of carrying out heating sticking by pressure with a hot calender roll is performed. Since this approach is established under heating pressurization, it is quick, moreover is very good, therefore it is very good. [ of fixing effectiveness ] [ of thermal efficiency ] However, while thermal efficiency is good in this hot calender roll method, in order that a hot calender roll front face and a toner may contact in the state of melting, a toner carries out adhesion transition on a hot calender roll front face, and there is a problem that this re-transfers and soils on the following covering sheet (offset phenomenon).

[0003] On the other hand, the copying machine points to the direction of improvement in the speed, the speed of a fixing roll also becomes quick inevitably, and the toner which can be established with short-time heating is demanded. Although it is thought that what is necessary is it to be required to be a quantity flow at the time of melting, and just to make small molecular weight of the resin used for a toner for that purpose in order to make it established as much as possible for a short time, the cohesive force of the resin by molecular weight fall is insufficient, and it becomes easy to generate an offset phenomenon conversely, and is not desirable. For this reason, although a fluidity usually falls victim to some extent, mixed use is carried out with the thing of low molecular weight, and the thing of the amount of macromolecules, and balance is given for the cohesive force which the thing of the amount of macromolecules has, and the fluidity which the thing of low molecular weight has. as such an example — for example, a Japanese Patent Publication No. 55-No. 6895 official report, JP,63-32180,B, and USP 4,921,771 etc. — the starting technique is proposed. However, to improvement in the speed, it is not yet enough and there is a case where it corresponds by amelioration of a machine etc., plentifully. That is, the silicone oil was applied in cloth or paper on the surface of the hot calender roll, and offset is prevented. In this case, since a facility of a machine becomes complicated, repair of a machine and management become complicated, lead to a cost rise, and are not desirable. Therefore, development of the toner for fixing (oilless fixing method) which is a toner for high-speed machines, and does not need use of oil, such as a silicone oil, is desired. Moreover, a manuscript becomes very beautiful with the rise of the printer engine performance, and the appearance of the copying machine which can reproduce a manuscript as faithfully as possible has also come to be required strongly. the size completely same as a line a deep line a thick thin line is thick and thin [ a line ] and thin is thin, and deep [ a line ] and very thin — it is required for the same form to reproduce a manuscript as faithfully as possible, and, for that, it can reappear also by the very fine line — as — the particle size of a toner — small — it is necessary to carry out — the diameter-sized toner of a granule — \*\*\*\* — last — it is becoming like. However, a thin line becomes thick and is not desirable, if a toner is crushed and it spreads greatly with a hot calender roll at the time of fixing, even if it uses the diameter-sized toner of a granule with much trouble. Moreover, the high-definition toner is desired for the flare of the toner when being fixed to paper to be able to maintain the magnitude of the original toner as much as possible with high resolution.

[0004]

[Problem(s) to be Solved by the Invention] Although what is necessary is to crush a toner with a hot calender roll, to make [ many / as possible ] the amount of macromolecules at the time of fixing in order not to spread greatly and to carry out, and just to give elasticity to a toner, productivity is downed that it is hard to grind in that case, and it becomes a problem. Moreover, although generally moreover diameter[ of a granule ]-ized to about 7micro at high resolution to make it a high-definition toner, in order to make it easy to grind, if low molecular weight is increased, fines will carry out abundant generating at the time of grinding, productive efficiency falls, and a production cost goes up sharply and poses a problem.

[0005] On the other hand, many toners using crosslinked polymer as the offset prevention approach in development of the toner for oilless fixing methods are also proposed. For example, the approach using the crosslinked polymer

manufactured by the emulsion-polymerization method is indicated by JP,60-36582,B. In this case, it was very difficult for offset-proof nature not to become good although a grindability will become good, if a grindability gets worse and the amount of another side crosslinked polymer decreases, although offset-proof nature will become good, if the crosslinked polymer used contains a part for gel 50 to 99% and a part for this gel is made [ many ], but to satisfy both offset-proof nature and grindability. Moreover, in order to stabilize an emulsification particle at the time of crosslinked polymer manufacture, it is necessary to make a dispersant and a distributed assistant use together by this approach. Since it has a bad influence on an electrical property, especially charge stability in order that these dispersants may tend to absorb moisture, it is necessary to remove these as much as possible after crosslinked polymer manufacture. However, an effort great for washing these and removing completely is required, and the displacement of wash water also increases and the processing is also serious. moreover, USP 4,966,829 a number official report — a gel component — 0.1 – 60 percentage-by-weight implication and tetrahydrofuran extractives — setting — the molecular weight of the Maine peak — the molecular weight of 1,000–25,000 and a subpeak, or a shoulder — 3,000–150,000 the toner containing the vinyl system polymer which it has at least one is good — the purport indication is carried out. However, the method of manufacturing this was the suspension method, and since the dispersant and the distributed assistant were made to use together like an emulsion-polymerization method also in this case at the time of manufacture, there was the completely same problem as the above-mentioned emulsion polymerization. It is resin (USP 4,963,456) according to a solution-polymerization method as resin for toners with fixable [ sufficient / this invention person etc. ] this sake. It has developed.

[0006] Although the resin by the solution polymerization method removes the solvent after polymerization termination, since all low volatile components, such as an unreacted residual monomer and a decomposition product of an initiator, can be distilled off at this time, it is thought with very few impurities that stable homogeneous resin is obtained electrically and the optimal thing for toners is obtained. However, manufacture of the crosslinked polymer by the solution polymerization method had a problem of it becoming impossible for the wye ZEMBERUGU effectiveness (for resin to coil around a stirring rod) to occur and manufacture. Therefore, this invention person etc. is the approach of macromolecule-izing as much as possible with bulk etc. further (USP 5,084,368). It developed. However, a limitation is one of the things of the amount of macromolecules which can be manufactured, and it had not resulted till the place which conquers offset nature completely. Moreover, in JP,60-38700,B, it is a glycidyl group content monomer 3 – 40% Copolymer which it has (A) Cross-linking compound (B) The toner of reverse charge was generated by the long-term test of that the toner binder which carried out [ the binder ] heating mixing and was manufactured is good although the purport indication is carried out, since an epoxy group is as abundant \*\* in this toner, and a toner which has produced the problem in endurance and is not necessarily satisfied at it was not developed.

[0007]

[Means for Solving the Problem] As a result of inquiring wholeheartedly that these demands should be satisfied, by making a bridge construct by the specific ratio using the compound which has the resin and the glycidyl group of the specification manufactured by the solution polymerization method, this invention persons can respond to a high-speed machine, and develop the technique of obtaining the toner which are moreover high resolution and high definition, and was excellent in the grindability. That is, this invention is 0 for electrophotography which consists of a coloring agent, a binder, and an electric charge regulator at least. In NA this binder — (number-average-molecular-weight Mn) 1,000 –20,000 and the acid number 5.0–100 it is — Per 1Eq of COOH radicals in the COOH content vinyl resin (A) whose Tg point is 40–75 degrees C, and this COOH content vinyl resin (A), and as a glycidyl group 0.05–1.0 It is the toner for electrophotography characterized by consisting of glycidyl compounds (B) which have the equivalent. furthermore — as a coloring agent, an electric charge regulator, and a binder — number average molecular weight 1,000–20,000 and the acid number 5.0–100 it is — And it is 0.05–1.0 as a glycidyl group per 1Eq of COOH radicals in the COOH content vinyl resin (A) whose Tg point is 40–75 degrees C, and this COOH content vinyl resin (A). Melting kneading of the constituent using the glycidyl compound (B) which has the equivalent is carried out. It is also the manufacturing method of the toner for electrophotography characterized by pulverizing the obtained kneading object.

[0008] As a COOH content vinyl monomer used for manufacture of the COOH content vinyl resin (A) used in this invention An acrylic acid, a methacrylic acid, a maleic anhydride, a maleic acid, boletic acid, A cinnamon acid, boletic acid methyl, boletic acid ethyl, boletic acid propyl, Boletic acid butyl, boletic acid octyl, maleic-acid methyl, maleic-acid ethyl, The resin which was chosen from COOH content vinyl monomers, such as monoester of partial saturation dibasic acids, such as maleic-acid propyl, maleic-acid butyl, and maleic-acid octyl, and which was obtained by copolymerizing a kind with the following vinyl monomer at least is used. As a COOH content vinyl monomer and a vinyl monomer to copolymerize For example, styrene, such as styrene, P-methyl styrene, alpha methyl styrene, and vinyltoluene A methyl acrylate, an ethyl acrylate, acrylic-acid propyl, butyl acrylate, Acrylic-acid octyl, acrylic-acid cyclohexyl, acrylic-acid stearyl, Acrylic-acid benzyl, acrylic-acid furfuryl, acrylic-acid hydroxyethyl, Acrylic ester, such as acrylic-acid hydroxy butyl, acrylic-acid dimethyl aminomethyl, and acrylic-acid dimethylaminoethyl Methacrylic acid methyl, methacrylic acid ethyl, methacrylic acid propyl, Methacrylic acid butyl, methacrylic acid octyl, methacrylic acid cyclohexyl, Methacrylic acid stearyl, methacrylic acid benzyl, methacrylic acid furfuryl, Methacrylic acid hydroxyethyl, methacrylic acid hydroxy butyl, Methacrylic acid ester, such as methacrylic acid dimethyl aminomethyl and methacrylic acid dimethylaminoethyl Boletic acid dimethyl, boletic acid dibutyl, boletic acid dioctyl, The diester of partial saturation dibasic acids, such as maleic-acid dimethyl, dibutyl maleate, and dioctyl maleate There are acrylonitrile, meta-acrylonitrile, acrylamide, meta-acrylamide, N permutation

acrylamide, N permutation meta-acrylamide, an amide of a kind, etc., and at least one sort of these vinyl monomers is used. As a vinyl monomer especially desirable in these, they are styrene, acrylic ester, methacrylic acid ester, boleic acid dialkyl ester, acrylonitrile, acrylamide, methacrylamide, etc.

[0009] COOH content vinyl resin (A) has desirable resin (number-average-molecular-weight Mn) 1,000 – 20,000 and whose Tg point are 40–75 degrees C. Number average molecular weight is 1,000. Below, Tg point becomes 40 degrees C or less, blocking is caused, preferably, a fluidity worsens [ number average molecular weight ] or more by 20,000, and fixable gets worse. Moreover, energy great for a grindability especially getting very bad and making it 7micro is required, and productivity does not bear practicality bad. If Tg point becomes 75 degrees C or more, softening temperature will go up, fixable gets worse, and the toner of this purpose is not obtained. The COOH content in COOH content vinyl resin (A) has good 5.0 – 100 KOHmg/g as the acid number, and its 10 – 80 KOHmg/g is especially desirable. If the acid number separates from this range, a problem will appear in a grindability. By 100 or more KOHmg/g, a lifting fluidity gets worse [ especially the acid number / most ] gelation, and a problem appears also in fixable.

[0010] The glycidyl ester content vinyl resin whose weight average molecular weight is 3,000–10,000 and whose epoxy value is 0.01–0.2Eq / 100g as a glycidyl compound (B) in this invention is desirable. Glycidyl ester content vinyl resin is resin with the vinyl monomer of at least a kind of and others of vinyl monomers, such as the vinyl monomer containing a glycidyl group, for example, metaglycidyl acrylate, acrylic-acid beta methyl glycidyl, metaglycidyl acrylate, and methacrylic acid beta methyl glycidyl, copolymerized and obtained. Weight average molecular weight is 3,000. Below, even if it constructs a bridge, it can hardly thicken, and offset-proof nature cannot be improved. Conversely, 10,000 or more are in the middle of bridge formation, since the compatibility of a bridge formation object gets worse and the bridge formation object carries out a separation deposit into resin, it does not thicken, and offset nature does not become good. Moreover, the thing of epoxy value of 0.01–0.2Eq / the range of 100g is desirable. 0. 01Eq / 100g If it is in below, thickening hardly takes place and amelioration of offset nature cannot be performed. 0.2 Eq / 100g Above, since the compatibility of a bridge formation object gets worse and the bridge formation object carries out a separation deposit into resin, it does not thicken, although gel is generated and offset nature does not become good, either.

[0011] It sets to this invention and, for the operating rate of COOH content vinyl resin (A) and a glycidyl compound (B), the glycidyl group in a glycidyl compound is 0.05–1.0 to 1Eq of COOH radicals in COOH content vinyl resin (A). It uses so that it may become the equivalent. The effectiveness made into the purpose of this invention in 0.05 or less equivalence is not discovered, but it is 1.0. Above equivalence, charge is changed at the time of a long-term torture test, and it is not desirable. Moreover, as the manufacture approach of COOH content vinyl resin (A), solution polymerization is desirable, and raises and explains how to build the resin of the above molecular weight for an example below, aromatic hydrocarbon, such as benzene, toluene, ethylbenzene, a xylene, and cumene, Solvesso #100, and #150 (trade name made from the Esso chemistry) etc. — keeping temperature and internal pressure constant in the proof-pressure container which taught the solution in which homogeneity carries out dissolution mixing of one or more solvents, vinyl monomers, and polymerization initiators beforehand to filled-liquid with the solvent from inside, it supplies continuously and a polymerization is performed. A flash plate is carried out to the vacuum system of about 0 – 200 mmHg more nearly continuously than the time of being in a steady state, a solvent etc. is distilled off, vinyl resin and a solvent are separated, and solid vinyl resin is obtained.

[0012] The various approaches shown below can be taken about the mode using the binder, the COOH content vinyl resin (A), and the glycidyl compound (B) by which it is characterized [ of this invention ].

\*\* How to add a bulking agent required for toners, such as a coloring agent and an electric charge regulator, and use as a toner, after using after mixing, a biaxial kneading machine, etc. with a Henschel mixer, making COOH content vinyl resin (A) carry out melting kneading of the glycidyl compound (B) at the temperature of 150–220 degrees C and making the reaction of a COOH radical and a glycidyl group fully perform to it.

\*\* The approach to which COOH content vinyl resin (A) and a glycidyl compound (B) are made to react at the time of a toner chemically-modified [ which carries out melting kneading at the temperature of 150–220 degrees C after mixing using a biaxial kneading machine etc. enough together with a bulking agent required for toners, such as a coloring agent and an electric charge regulator, ] degree with an unreacted condition.

COOH content vinyl resin (A) and a glycidyl compound (B) \*\* With an unreacted condition, Together with a bulking agent required for toners, such as a coloring agent and an electric charge regulator, enough After mixing. Carry out melting kneading at the temperature of 110–140 degrees C using a biaxial kneading machine etc., and it is not made to almost react at the time of this melting kneading, but there is the approach of making it 150–220 degrees C, and making it react etc. at the time of fixing of a copying machine, and temperature of a hot calender roll may be performed by which approach at it.

[0013] In this invention, the well-known dyes and pigments generally used can be used as a coloring agent used. For example, carbon black, acetylene black, lamp black, Black pigments, such as magnetite, the chrome yellow, Synthetic Ochre, the HAIZA yellow G A quinoline yellow lake, the permanent yellow NCG, a molybdenum orange, Balkan Peninsula Orange, indanthrene, brilliant Orange GK, red ocher, Brilliant carmine 6B, a BURIZA phosphorus lake, Violet Lake, Magnetic powder, such as the fast violet B, cobalt blue, an alkali blue lake, a copper phthalocyanine blue, fast-sky-blue NEPIGUMENTO Green B, the Malachite Green lake, titanium oxide, a zinc white, magnetite, and a soft ferrite, etc. is mentioned. The amount used is 0.1 usually used – 20 weight sections.

[0014] In this invention, the mixed use of a part of other resin, for example, polyester resin, polyamide resin, vinyl chloride resin, polyvinyl butyral resin, styrene butadiene resins, coumarone-indene resin, melamine resin, polyolefin

resin, etc., can be carried out in the range which does not check the purpose of this invention. Moreover, the well-known electric charge regulator which makes the start Nigrosine, quaternary ammonium salt, and metal-containing azo dye can be used choosing it suitably, and the amount used is 0.1 usually used - 10 weight sections.

[0015] In this invention, any well-known approaches are conventionally employable as an approach of making a toner. For example, the premix of resin, a coloring agent, an electric charge regulator, the wax, etc. is carried out beforehand, and subsequently, after [ heating melting kneading ] cooling grinding is carried out, and it classifies with a biaxial kneading machine, and is abbreviation. It is made a 7-micron particle. The number average molecular weight and the weight average molecular weight in this invention are that for which it asked by the GPC method, and are the conversion molecular weight which created the calibration curve with mono dispersion standard polystyrene. A Measuring condition is as follows.

GPC equipment; JASCO TWINCLE HPLCDETECTOR ; SHODEX RI SE-31COLUMN ; SHODEX GPCA-80M\*2+KF-802 \*\* Intermediation ; TETRAHYDROFURAN style \*\* ; 1.2ml/min.[0016]

[Example] Next, an example explains this invention concretely. In addition, henceforth, especially the "section" expresses the weight section, unless it refuses.

[The example of manufacture of COOH content vinyl resin (A)]

The example of manufacture 1 styrene 60.3 section, and acrylic-acid n-butyl 6.3 The section and methacrylic acid 2.8 It is styrene 100 to the solution which consists of the section and the xylene solvent 30 section. Per [ 0.6 ] section G t of the section - About what dissolved butyl peroxide in homogeneity, it is internal temperature 190 \*\* internal pressure. By 750 cc/hr. the 5l. reactor held to 6kg/cm<sup>2</sup> was supplied continuously, the polymerization was carried out to it, and low-molecular-weight polymerization liquid was obtained. The flash plate of this was carried out into the bessel of 190 \*\*10mmHg, and the solvent etc. was distilled off. The acid number whose Tg the number average molecular weight of the obtained vinyl resin was 5200, and was 65 degrees C was 26.

[0017] It is polymerization temperature in case low-molecular-weight polymerization liquid is manufactured in the example 2 of manufacture, and the example 1 of 3 manufactures. 190 degrees C 180 degrees C reaches. Vinyl resin was completely obtained like the example 1 of manufacture except having considered as 220 degrees C. Although obtained, the physical-properties value was shown in Table -1.

[0018] It is polymerization temperature in case low-molecular-weight polymerization liquid is manufactured in the example 1 of example of manufacture 4 manufacture. 190 degrees C Vinyl resin was completely obtained like the example 1 of manufacture except having considered as 160 degrees C. Although obtained, the physical-properties value was shown in Table -1.

[0019] It sets for the example 1 of example of manufacture 5 manufacture, and they are the styrene 60.3 section and acrylic-acid n-butyl 6.3 as a vinyl monomer. The section and methacrylic acid 2.8 They are the styrene 46.2 section, the methacrylic acid n-butyl 21 section, and methacrylic acid about the section. Vinyl resin was completely obtained like the example 1 of manufacture except having considered as the 2.8 sections. Although obtained, the physical-properties value was shown in Table -1.

[0020] It sets for the example 1 of example of manufacture 6 manufacture, and they are the styrene 60.3 section and acrylic-acid n-butyl 6.3 as a vinyl monomer. The section and methacrylic acid 2.8 They are the styrene 69.6 section and methacrylic acid about the section. Vinyl resin was completely obtained like the example 1 of manufacture except having considered as the 0.4 sections. Although obtained, the physical-properties value was shown in Table -1.

[0021] It sets for the example 1 of example of manufacture 7 manufacture, and they are the styrene 60.3 section and acrylic-acid n-butyl 6.3 as a vinyl monomer. The section and methacrylic acid 2.8 They are the styrene 64.1 section and acrylic-acid n-butyl 4.2 about the section. The section, methacrylic acid Vinyl resin was completely obtained like the example 1 of manufacture except having considered as the 1.8 sections. Although obtained, the physical-properties value was shown in Table -1.

[0022] It sets for the example 1 of example of manufacture 8 manufacture, and they are the styrene 60.3 section and acrylic-acid n-butyl 6.3 as a vinyl monomer. The section and methacrylic acid 2.8 They are the styrene 51.8 section, the acrylic-acid n-butyl 12.6 section, and methacrylic acid about the section. Vinyl resin was completely obtained like the example 1 of manufacture except having considered as the 5.6 sections. Although obtained, the physical-properties value was shown in Table -1.

[0023] It sets for the example 1 of example of manufacture 9 manufacture, and they are the styrene 60.3 section and acrylic-acid n-butyl 6.3 as a vinyl monomer. The section and methacrylic acid 2.8 Vinyl resin was completely obtained like the example 1 of manufacture except having made the section into the styrene 38.5 section, the acrylic-acid n-butyl 17.5 section, and the methacrylic acid 14 section. Although obtained, the physical-properties value was shown in Table -1.

[0024] The vinyl resin 86 section and PD6300 (styrene acrylic resin containing a glycidyl group, epoxy value 0.19 eq /g [ 100 ], weight average molecular weight = 8, 000, Tg= degrees C [ 52 ], Mitsui Toatsu Chemicals make) which were obtained in the example 1 of example 1 manufacture They are after mixing and a biaxial kneading machine (PCM-30 mold, Ikegai make) with a Henschel mixer about the ten sections. The kneading reaction was carried out by 200 \*\*. after cooling / grinding and carbon black MA100(Mitsubishi Kasei make) 8 the section and a polypropylene wax (bis-call 550 P) — 5 as the section and an electric charge regulator — eye ZENSU pyrone black TRH 1 section addition — carrying out — again — a Henschel mixer — after mixing and biaxial kneading machine (PCM-30 a mold, Ikegai make) It was made to knead by 170 \*\*. Subsequently, it cools, grinds and classifies and is abbreviation. The 7-micron toner was obtained. Mix this toner 3 section and the carrier 97 section, consider as a developer, convert a

commercial high-speed copying machine, an image is made to write, it evaluates as a toner, and a result is shown in Table -1.

[0025] The vinyl resin obtained in the example 1 of example 2 manufacture was replaced with the vinyl resin obtained in the example 2 of manufacture, and also a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0026] The vinyl resin obtained in the example 1 of example 3 manufacture was replaced with the vinyl resin obtained in the example 3 of manufacture, and also a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0027] The vinyl resin obtained in the example 1 of example 4 manufacture was replaced with the vinyl resin obtained in the example 5 of manufacture, and also a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0028] It sets in the example 5 example 1, and they are PDs 6300 and 10. It is the section 5 Except having made it the section, a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0029] It sets in the example 6 example 1, and is PD6100 (styrene-acrylic resin containing a glycidyl group, epoxy value 0.10 eq /g [ 100 ], weight average molecular weight = 8,000, Tg= degrees C [ 56 ], Mitsui Toatsu Chemicals make) about PD6300. Except having carried out, a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0030] the vinyl resin 86 section and PDs 6300 and 10 which were obtained in the example 1 of example 7 manufacture The section and carbon black MA100(Mitsubishi Kasei make) 8 the section and a polypropylene wax (bis-call 550 P) — 5 as the section and an electric charge regulator — cetyl trimethyl AMMONIUM star's picture the two sections — a Henschel mixer — after mixing and biaxial kneading machine (PCM-30 a mold, Ikegai make) It was made to knead by 150 \*\*. Subsequently, it cools, grinds and classifies and is abbreviation. The 7-micron toner was obtained. This toner 3 Mix the section and the carrier 97 section, consider as a developer, convert the commercial high-speed copying machine using + charge toner, an image is made to write, it evaluates like an example 1, and a result is shown in Table -1.

[0031] To the vinyl resin obtained in the example 7 of manufacture in the vinyl resin obtained in the example 1 of example 8 manufacture, they are PDs 6300 and 10 further. The section was changed to the 6.3 sections, and also image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0032] To the vinyl resin obtained in the example 8 of manufacture in the vinyl resin obtained in the example 1 of example 9 manufacture, it is . PDs 6300 and 10 The section was changed to the 20 sections, and also image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0033] Using the vinyl resin obtained in the example 1 of example of comparison 1 manufacture, a glycidyl compound is not used, and also a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0034] The vinyl resin obtained in the example 1 of example of comparison 2 manufacture was replaced with the vinyl resin obtained in the example 4 of manufacture, and also a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0035] The vinyl resin obtained in the example 1 of example of comparison 3 manufacture was replaced with the vinyl resin obtained in the example 6 of manufacture, and also a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0036] The vinyl resin obtained in the example 1 of example of comparison 4 manufacture was replaced with the vinyl resin obtained in the example 7 of manufacture, and also a toner is obtained completely like an example 1, image evaluation is carried out completely like an example 1, and a result is shown in Table -1.

[0037] [The evaluation approach of a toner]

1) Fixable; copy with a commercial high-speed copying machine (72 copy speed for \*\*/), and it is a rubber about between this part for solid Kurobe and white ground that were copied. (plastics rubber "MONO" by the dragonfly pencil company) It is 100 at the fixed force. The time round trip was carried out, the blackness for solid Kurobe was measured with the ink concentration meter, and the residual ratio of a toner was expressed with the ratio of concentration.

2) Offset nature; it is continuation 100 with a commercial high-speed copying machine (72 copy speed for \*\*/). The \*\* copy was carried out and the existence of offset generating at that time was investigated.

[0038] O; — offset — all — not \*\*\*\*\*ing — \*\*; offset — small — generating x; offset — extent of condensation of fine particles after leaving a generating 3 blocking nature; polymerization toner for one week completely under the environment of the temperature of 50 degrees C and 50% of relative humidity was measured as follows visually.

O; — O; which is not condensed at all, although condensed slightly x with the aggregate which does not get loose even if it shakes well \*\*; container which will get loose if a container is shaken lightly; A toner is established with the high-speed copying machine (72 copy speed for \*\*/) of 4 image-quality repeatability; marketing nodule-ized completely. The magnitude of the toner before and behind fixing was observed under the microscope, and it asked for to what time of the original toner the magnitude after fixing turned.

5) Grindability; a part of thing cooled after biaxial kneading was extracted and ground at the time of toner manufacture, step was kept with the grain size of the 28 mesh-on of 16-mesh undershirts, and the jet mill ground. Particle size distribution are searched for for a rate with a measurement and a grain size of 5-10micro with a Coulter counter.

O; 85% It is O;70-85% \*\*;50-70% x;50% above. The 50,000-sheet continuation copy test was carried out below with the high-speed copying machine (72 copy speed for \*\*/) of 6 endurance marketing, the pattern was copied, and the difference in image quality was checked for repeatability before and after the check and the continuation test. O Thing x to which the thing \*\*; continuation test back ID which does not almost have a difference before and behind; was downed greatly; fogging occurred and image quality was confused greatly.

[0039]

[Table 1]

[0040]

[Effect of the Invention] As shown in Table -1, it can respond to a high-speed machine well, by the approach of this invention, moreover it is high resolution and excels in image quality, and a grindability is also good and it has the practically excellent engine performance.

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[Translation done.]

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(54)【発明の名称】 電子写真用トナー

(57)【要約】

【構成】 数平均分子量 ( $M_n$ ) 1,000 ~20,000、酸価 5.0 ~100 であり、かつ  $T_g$  点が 40 ~75°C である  $COOH$  含有ビニル樹脂 (A) と該  $COOH$  含有ビニル樹脂 (A) 中の  $COOH$  基 1 当量当りグリシジル基として 0.05 ~1.0 当量を有するグリシジル化合物 (B) より構成されている電子トナー。

【効果】 高速機によく対応でき、しかも高解像度で且つ画質に優れしており、粉碎性も良好で、実用上優れた性能を有している。

## 【特許請求の範囲】

【請求項1】 少なくとも着色剤と結着剤と荷電調整剤からなる電子写真用トナーにおいて、該結着剤が数平均分子量 (Mn) 1,000 ~20,000、酸価5.0 ~100 であり、かつTg点が40 ~75°CであるCOOH含有ビニル樹脂 (A) と該COOH含有ビニル樹脂 (A) 中のCOOH基1当量当りグリシジル基として0.05~1.0当量を有するグリシジル化合物 (B) より構成されていることを特徴とする電子写真用トナー。

【請求項2】 該結着剤がCOOH含有ビニル樹脂 (A) とグリシジル化合物 (B) とを反応せしめた樹脂組成物である請求項1記載の電子写真用トナー。

【請求項3】 COOH含有ビニル樹脂 (A) が、アクリル酸、メタクリル酸、無水マレイン酸、マレイン酸、フマール酸、ケイヒ酸、不飽和二塩基酸のモノエステル類から選ばれた少なくとも一種を共重合して得られたものである請求項1記載の電子写真用トナー。

【請求項4】 COOH含有ビニル樹脂 (A) が、ステレン類、アクリル酸エステル類、メタアクリル酸エステル類、フマール酸ジアルキルエステル類、アクリロニトリル、アクリルアミド、メタクリルアミドから選ばれた少なくとも一種のビニル単量体を共重合して得られたものである請求項1記載の電子写真用トナー。

【請求項5】 グリシジル化合物 (B) が、重量平均分子量3,000 ~10,000で且つエポキシ価0.01~0.3Eq/100gであるグリシジルエステル含有樹脂である請求項1記載の電子写真用トナー。

【請求項6】 COOH含有ビニル樹脂 (B) が、溶液重合法により製造されたものである請求項1記載の電子写真用トナー。

【請求項7】 少なくとも着色剤と結着剤と荷電調整剤とを溶融混練し、得られた混練物を微粉碎して得られた電子写真用トナーに於いて、該結着剤がCOOH含有ビニル樹脂 (A) とグリシジル化合物 (B) とを上記溶融混練時に架橋反応せしめたものである電子写真用トナーの製造法。

## 【発明の詳細な説明】

### 【0001】

【産業上の利用分野】 本発明は電子写真、静電記録、静電印刷などに於ける、静電荷像を現像するための電子写真用トナーに関する。さらに詳しくは高速機に対応でき、しかも高解像度・高画質で且つ粉碎性に優れた電子写真用トナーに関する。

### 【0002】

【従来の技術】 一般に、PPC複写機やプリンターに於ける電子写真用法は、光感光体上に静電気的潜像を形成し、ついで該潜像をトナーを用いて現像し、紙等の被定着シート上にトナー画像を転写した後、熱ロールで加熱圧着する方法が行われている。この方法は、加熱加圧下で定着を行うので迅速でしかも熱効率が極めて良好であ

り、従つて定着効率が非常に良い。しかしながら、この熱ロール方式に於いては熱効率が良い反面、熱ロール表面とトナーが溶融状態で接触するため、トナーが熱ロール表面に付着転移し、次の被着シートにこれが再転移して汚す（オフセット現象）という問題がある。

【0003】 一方、複写機は、高速化の方向を指向しており、必然的に定着ロールのスピードも速くなり、短時間の加熱で定着出来るトナーが要求されている。出来るだけ短時間で定着させる為には溶融時高流動であることが必要で、そのためにはトナーに用いられる樹脂の分子量を小さくすれば良いと考えられているが、分子量低下による樹脂の凝集力が不足し、逆にオフセット現象が発生し易くなり、好ましくない。この為通常、流動性はある程度犠牲になるが、低分子量のものと高分子量のものと混合使用して、高分子量のものが有する凝集力と低分子量のものが有する流動性とでバランスを持たしている。このような例として、例えば、特公昭55-6895号公報、特公昭63-32180号公報、USP 4,921,771 等に係る技術が提案されている。しかし、高速化に対しては、いまだ充分ではなく、機械の改良等で対応している場合が多くある。即ち、熱ロールの表面に布や紙でシリコンオイルを塗布してオフセットを防止している。この場合、機械の設備が複雑になるため、機械の補修、管理が複雑になり、コストアップに繋がり、好ましくない。したがつて高速機用トナーで、且つシリコンオイル等のオイルの使用を必要としない定着用トナー（オイルレス定着方式）の開発が望まれている。又、プリンター性能のアップと共に原稿が非常に綺麗になり、原稿を出来るだけ忠実に再現出来るような複写機の出現も強く要求されるようになって来た。太い薄い線は太く薄く、細い濃い線は細く濃く、非常に細い線も全く同じ太さ同じ形に、原稿を出来るだけ忠実に再現することが必要で、この為には、非常に細かい線でも再現出来るようトナーの粒径も小さくする必要があり小粒径化トナーが要求されるようになってきた。しかし、折角小粒径化トナーを用いても、定着時熱ロールでトナーが潰されて大きく拡がってしまっては、細線が太くなり好ましくない。紙に定着した時のトナーの拡がりは出来るだけ元のトナーの大きさを維持できるよう高解像度でしかも高画質のトナーが熱望されている。

### 【0004】

【発明が解決しようとする課題】 定着時熱ロールでトナーが潰されて大きく拡がらなくするためには、高分子量を出来るだけ多くしトナーに弾性を持たせればよいが、その場合粉碎し難く生産性がダウンし問題となる。また、高解像度でしかも高画質のトナーにするには一般に7μ位に小粒径化するのであるが、粉碎し易くするため、低分子量を増やすと粉碎時微粉が多量発生し、生産効率が落ち生産コストが大幅に上昇し問題となる。

【0005】 一方、オイルレス定着方式用トナーの開発

に於けるオフセット防止方法としては架橋ポリマーを用いたトナーも数多く提案されている。例えば特公昭60-36582号公報等には、乳化重合法で製造された架橋ポリマーを用いる方法が開示されている。この場合、用いられる架橋ポリマーはゲル分を50～99%含有しており、このゲル分を多くすると、耐オフセット性は良くなるが粉碎性は悪化し、他方架橋ポリマー分が少なくなると粉碎性はよくなるが耐オフセット性は良くならず、耐オフセット性と粉碎性の両者を満足することは極めて困難であった。また、この方法では架橋ポリマー製造時に乳化粒子を安定化させるため分散剤や分散助剤を併用させる必要がある。これら分散剤は吸湿し易いため電気特性、特にチャージ安定性に悪影響を及ぼすので、架橋ポリマー製造後、できるだけこれらを取り除く必要がある。しかし、これらを洗浄して完全に取り除くには多大の労力が必要であり、また、洗浄水の排水量も多くなりその処理も大変である。また、USP 4,966,829号公報には、ゲル成分が0.1～60重量パーセント含み且つテトラヒドロフラン可溶分に於いてメインピークの分子量が1,000～25,000、且つ、サブピーク又はショルダーの分子量が3,000～150,000が少なくとも一つ有するビニル系重合体を含有するトナーが良い旨開示されている。しかし、これを製造する方法はサスペンション法であり、この場合も乳化重合法と同じように、製造時に分散剤や分散助剤を併用させて、上記乳化重合と全く同じ問題があった。この為、本発明者等は定着性の良いトナー用樹脂として、溶液重合法による樹脂(USP 4,963,456)を開発してきた。

【0006】溶液重合法による樹脂は、重合終了後溶剤を除去するが、この時、未反応の残存モノマーや開始剤の分解物等低揮発成分は全て留去出来るので、非常に不純物の少ない電気的には安定な均質な樹脂が得られ、トナー用には最適のものが得られるものと考えられる。しかしながら、溶液重合法による架橋ポリマーの製造は、ワイゼンベルグ効果(攪拌棒に樹脂が巻きつく)が発生し製造出来なくなるという問題があった。したがって、本発明者等は、さらにバルク等で出来るだけ高分子化する方法(USP 5,084,368)を開発した。しかし製造出来る高分子量のものには限界があり、オフセット性を完全に克服するところまでは至っていなかった。また、特公昭60-38700には、グリシジル基含有単量体を3～40%有する共重合体(A)と架橋性化合物(B)とを加熱混合して製造したトナーバインダーが良い旨開示されているが、このトナーに於いてはエポキシ基が多量残っているため長期のテストで逆チャージのトナーが発生し耐久性に問題を生じており、必ずしも満足するようなトナーは開発されていなかった。

#### 【0007】

【課題を解決するための手段】本発明者らは、これらの要求を満足すべく鋭意検討した結果、溶液重合法にて製

造した特定の樹脂とグリシジル基を有する化合物を用いて特定の比率で架橋させることにより、高速機に対応でき、しかも高解像度・高画質で且つ粉碎性に優れたトナーを得る技術を開発したものである。即ち、本発明は、少なくとも着色剤と結着剤と荷電調整剤からなる電子写真用トナーにおいて、該結着剤が数平均分子量(Mn)1,000～20,000、酸価5.0～100であり、かつTg点が40～75℃であるCOOH含有ビニル樹脂(A)と該COOH含有ビニル樹脂(A)中のCOOH基1当量当たりグリシジル基として0.05～1.0当量を有するグリシジル化合物(B)より構成されていることを特徴とする電子写真用トナーである。さらには、着色剤と荷電調整剤及び結着剤として数平均分子量1,000～20,000、酸価5.0～100であり、かつTg点が40～75℃であるCOOH含有ビニル樹脂(A)と該COOH含有ビニル樹脂(A)中のCOOH基1当量当たりグリシジル基として0.05～1.0当量を有するグリシジル化合物(B)を用いた組成物を溶融混練し、得られた混練物を微粉碎することを特徴とする電子写真用トナーの製造法もある。

【0008】本発明に於いて使用されるCOOH含有ビニル樹脂(A)の製造に用いられるCOOH含有ビニル単量体としては、アクリル酸、メタクリル酸、無水マレイン酸、マレイン酸、フマール酸、ケイヒ酸、フマール酸メチル、フマール酸エチル、フマール酸プロピル、フマール酸ブチル、フマール酸オクチル、マレイン酸メチル、マレイン酸エチル、マレイン酸プロピル、マレイン酸ブチル、マレイン酸オクチル等の不飽和二塩基酸のモノエステル類等のCOOH含有ビニル単量体から選ばれた少なくとも一種を下記ビニル単量体と共に重合して得られた樹脂が用いられる。COOH含有ビニル単量体と共に重合するビニル単量体としては、例えば、スチレン、P-メチルスチレン、α-メチルスチレン、ビニルトルエン等のスチレン類、アクリル酸メチル、アクリル酸エチル、アクリル酸プロピル、アクリル酸ブチル、アクリル酸オクチル、アクリル酸シクロヘキシル、アクリル酸ステアリル、アクリル酸ベンジル、アクリル酸フルフリル、アクリル酸ヒドロキシエチル、アクリル酸ヒドロキシブチル、アクリル酸ジメチルアミノメチル、アクリル酸ジメチルアミノエチル等のアクリル酸エステル類、メタアクリル酸メチル、メタアクリル酸エチル、メタアクリル酸プロピル、メタアクリル酸ブチル、メタアクリル酸オクチル、メタアクリル酸シクロヘキシル、メタアクリル酸ステアリル、メタアクリル酸ベンジル、メタアクリル酸フルフリル、メタアクリル酸ヒドロキシエチル、メタアクリル酸ヒドロキシブチル、メタアクリル酸ジメチルアミノメチル、メタアクリル酸ジメチルアミノエチル等のメタアクリル酸エステル類、フマール酸ジメチル、フマール酸ジブチル、フマール酸ジオクチル、マレイン酸ジメチル、マレイン酸ジブチル、マレイン酸ジオクチル等の不飽和二塩基酸のジエステル類、アクリロニトリル、

メタアクリロニトリル、アクリルアミド、メタアクリルアミド、N置換アクリルアミド、N置換メタアクリルアミド、類のアミド等があり、これらのビニル単量体の少なくとも1種が用いられる。これらの中で特に好ましいビニル単量体としてはステレン類、アクリル酸エステル類、メタアクリル酸エステル類、スマール酸ジアルキルエステル類、アクリロニトリル、アクリルアミド、メタクリルアミド等である。

【0009】COOH含有ビニル樹脂（A）は、数平均分子量（Mn）1,000～20,000、かつTg点が40～75℃である樹脂が好ましい。数平均分子量が1,000以下では、Tg点が40℃以下になりブロッキングを起こし好ましくなく、数平均分子量が20,000以上では、流動性が悪くなり定着性が悪化する。また、粉碎性が非常に悪くなり特に7μにするには多大のエネルギーが必要で生産性が悪く実用性に耐えない。Tg点が75℃以上になると軟化点が上昇し、定着性が悪化して本目的のトナーが得られない。COOH含有ビニル樹脂（A）中のCOOH含有量は、酸価として5.0～100KOHmg/gがよく、特に、10～80KOHmg/gが好ましい。酸価がこの範囲を外れると粉碎性に問題がでてくる。特に酸価が100KOHmg/g以上では、大部分がゲル化を起こし流動性が悪化し定着性にも問題がでてくる。

【0010】本発明に於けるグリシジル化合物（B）としては、重量平均分子量が3,000～10,000で且つエポキシ価が0.01～0.2Eq/100gであるグリシジルエステル含有ビニル樹脂が好ましい。グリシジルエステル含有ビニル樹脂は、グリシジル基を含有するビニル単量体、例えばアクリル酸グリシジル、アクリル酸βメチルグリシジル、メタアクリル酸グリシジル、メタアクリル酸βメチルグリシジル等のビニル単量体の少なくとも一種と他のビニル単量体との共重合して得られた樹脂である。重量平均分子量が3,000以下では、架橋しても殆ど増粘せず、耐オフセット性を改良する事はできない。逆に10,000以上でも、架橋途中で架橋体の相溶性が悪化し樹脂中にその架橋体が分離析出するので増粘せずオフセット性が良くならない。また、エポキシ価は0.01～0.2Eq/100gの範囲のものが好ましい。0.01Eq/100g以下にあっては増粘が殆ど起こらずオフセット性の改良は出来ない。0.2Eq/100g以上では、架橋体の相溶性が悪化し樹脂中にその架橋体が分離析出するのでゲルは生成するが増粘せずオフセット性も良くならない。

【0011】本発明に於いてはCOOH含有ビニル樹脂（A）とグリシジル化合物（B）との使用割合は、COOH含有ビニル樹脂（A）中のCOOH基1当量に対して、グリシジル化合物中のグリシジル基が0.05～1.0当量になるように用いる。0.05等量以下では本発明の目的とする効果が発現されず、1.0等量以上では長期耐久テスト時チャージが変動し、好ましくない。また、COOH含有ビニル樹脂（A）の製造方法としては、溶液重合

が好ましく、また、上述の様な分子量の樹脂を造る方法を下記に一例をあげて説明する。ベンゼン、トルエン、エチルベンゼン、キシレン、キュメン等の芳香族炭化水素、ソルベッソ#100、#150（エッソ化学製商品名）等の中から一つ以上の溶剤とビニル単量体と重合開始剤とを均一に溶解混合せしめた溶液を、予め溶剤で満液に仕込んだ耐圧容器に、温度と内圧を一定に保ちつつ連続的に供給して重合を行う。定常状態になった時より連続的に約0～200mmHgの真空系にフラッシュして溶剤等を留去してビニル樹脂と溶剤とを分離して、固形のビニル樹脂を得る。

【0012】本発明の特徴とする結着剤、COOH含有ビニル樹脂（A）及びグリシジル化合物（B）を用いる態様については次に示す種々の方法をとりうる。

① COOH含有ビニル樹脂（A）にグリシジル化合物（B）をヘンシェルミキサーで混合後、2軸混練機等を用いて150～220℃の温度で溶融混練させ、COOH基とグリシジル基との反応を充分に行わせた後に、着色剤や荷電調整剤等のトナーに必要な充填剤を添加してトナーにする方法。

② COOH含有ビニル樹脂（A）とグリシジル化合物（B）を未反応状態のまま、着色剤や荷電調整剤等のトナーに必要な充填剤と一緒に充分混合後、2軸混練機等を用いて150～220℃の温度で溶融混練させるトナー化工程時に反応させる方法。

③ COOH含有ビニル樹脂（A）とグリシジル化合物（B）を未反応状態のまま、着色剤や荷電調整剤等のトナーに必要な充填剤と一緒に充分混合後、2軸混練機等を用いて110～140℃の温度で溶融混練させ、この溶融混練時には殆ど反応させず、複写機の定着時に熱ロールの温度を150～220℃にして反応させる方法等があり、いずれの方法で行っても良い。

【0013】本発明に於いて、使用される着色剤としては、一般に用いられている周知の染顔料が使用出来る。例えば、カーボンブラック、アセチレンブラック、ランプブラック、マグネタイト等の黒色顔料、黄鉛、黄色酸化鉄、ハイサイエローG、キノリンイエローレーキ、パーマネントイエローNCG、モリブデンオレンジ、バルカンオレンジ、インダンスレン、ブリリアントオレンジGK、ベンガラ、ブリリアントカーミン6B、ブリザリシレーキ、メチルバイオレットレーキ、ファストバイオレットB、コバルトブルー、アルカリブルーレーキ、フタロシアニンブルー、ファストスカイブルーネピグメントグリーンB、マラカイトグリーンレーキ、酸化チタン、亜鉛華、マグネタイトやソフトフェライト等の磁性粉等が挙げられる。使用量は通常用いられる0.1～20重量部である。

【0014】本発明に於いて、本発明の目的を阻害しない範囲に於いて、他の樹脂、例えばポリエステル樹脂・ポリアミド樹脂・塩ビ樹脂・ポリビニールブチラール樹

脂・スチレン-ブタジエン樹脂・クマロン-イソブテン樹脂・メラミン樹脂・ポリオレフィン樹脂等を一部混合使用出来る。また、ニグロシン、4級アンモニウム塩や含金属アゾ染料を初めとする公知の荷電調整剤を適宜選択して使用出来、使用量は通常用いられる0.1~10重量部である。

【0015】本発明に於いて、トナーを作る方法としては、従来公知のいかなる方法も採用出来る。例えば、樹脂・着色剤・荷電調整剤・ワックス等を予めプレミックスし、ついで2軸混練機で加熱溶融混練後冷却粉碎し分級して約7ミクロンの微粒子にする。本発明における数平均分子量や重量平均分子量はGPC法により求めたもので、単分散標準ポリスチレンで検量線を作成した換算分子量である。測定条件は下記の通り。

GPC装置: JASCO TWINCLE HPLC  
DETECTOR: SHODEX RI SE-31  
COLUMN: SHODEX GPCA-80M\*2+KF-802  
溶媒: TETRAHYDROFURAN  
流速: 1.2ml/min.

#### 【0016】

【実施例】次に実施例により本発明を具体的に説明する。なお、以降「部」は、特にことわらない限り重量部を表す。

#### 【COOH含有ビニル樹脂(A)の製造例】

##### 製造例1

スチレン60.3部、アクリル酸n-ブチル6.3部、メタアクリル酸2.8部とキシレン溶媒30部からなる溶液にスチレン100部当たり0.6部のジ-t-ブチルペーパーオキサイドを均一に溶解したものを、内温190℃内圧6kg/cm<sup>2</sup>に保持した5lの反応器に750cc/hrで連続的に供給して重合し低分子量重合液を得た。これを190℃10mmHgのベッセル中にフラッシュして溶剤等を留去した。得られたビニル樹脂の数平均分子量は5200であり、Tgは65℃であった、酸価は26であった。

##### 【0017】製造例2, 3

製造例1に於いて低分子量重合液を製造する際に重合温度190℃を180℃および220℃とした以外は全く製造例1と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

##### 【0018】製造例4

製造例1に於いて低分子量重合液を製造する際に重合温度190℃を160℃とした以外は全く製造例1と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

##### 【0019】製造例5

製造例1に於いてビニル単量体として、スチレン60.3部、アクリル酸n-ブチル6.3部、メタアクリル酸2.8部をスチレン46.2部、メタアクリル酸n-ブチル21部、メタアクリル酸2.8部とした以外は全く製造例1と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に

示した。

##### 【0020】製造例6

製造例1に於いてビニル単量体として、スチレン60.3部、アクリル酸n-ブチル6.3部、メタアクリル酸2.8部をスチレン69.6部、メタアクリル酸0.4部とした以外は全く製造例1と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

##### 【0021】製造例7

製造例1に於いてビニル単量体として、スチレン60.3部、アクリル酸n-ブチル6.3部、メタアクリル酸2.8部をスチレン64.1部、アクリル酸n-ブチル4.2部、メタアクリル酸1.8部とした以外は全く製造例1と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

##### 【0022】製造例8

製造例1に於いてビニル単量体として、スチレン60.3部、アクリル酸n-ブチル6.3部、メタアクリル酸2.8部をスチレン51.8部、アクリル酸n-ブチル12.6部、メタアクリル酸5.6部とした以外は全く製造例1と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

##### 【0023】製造例9

製造例1に於いてビニル単量体として、スチレン60.3部、アクリル酸n-ブチル6.3部、メタアクリル酸2.8部をスチレン38.5部、アクリル酸n-ブチル17.5部、メタアクリル酸14部とした以外は全く製造例1と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

##### 【0024】実施例1

製造例1で得られたビニル樹脂86部、PD6300(グリシジル基を含有したスチレン-アクリル系樹脂で、エポキシ価0.19eq/100g、重量平均分子量=8,000、Tg=52℃、三井東圧化学製)10部をヘンシェルミキサーにて混合後、2軸混練機(PCM-30型、池貝鉄工製)にて200℃で混練反応させた。冷却・粉碎後、カーボンブラックMA100(三菱化成製)8部、ポリプロピレンワックス(ビスコール550P)5部、荷電調整剤としてアイゼンスピロンブラックTRH1部添加し、再度ヘンシェルミキサーにて混合後、2軸混練機(PCM-30型、池貝鉄工製)にて170℃で混練させた。ついで冷却・粉碎・分級して約7ミクロンのトナーを得た。このトナー3部とキャリヤ97部とを混合して現像剤とし、市販の高速複写機を改造して、画像を書かせてトナーとして評価し結果を表-1に示す。

##### 【0025】実施例2

製造例1で得られたビニル樹脂を製造例2で得られたビニル樹脂に替えた他は実施例1と全く同様にしてトナーを得、実施例1と全く同様にして画像評価し結果を表-1に示す。

##### 【0026】実施例3

製造例1で得られたビニル樹脂を製造例3で得られたビ

ニル樹脂に替えた他は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0027】実施例 4

製造例 1 で得られたビニル樹脂を製造例 5 で得られたビニル樹脂に替えた他は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0028】実施例 5

実施例 1 に於いて、PD6300, 10 部を 5 部にした以外は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0029】実施例 6

実施例 1 に於いて、PD6300 を PD6100 (グリシジル基を含有したスチレンーアクリル系樹脂で、エポキシ価 0.10eq /100g, 重量平均分子量 = 8,000, Tg = 56°C, 三井東圧化学製) にした以外は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0030】実施例 7

製造例 1 で得られたビニル樹脂 86 部、PD6300, 10 部、カーボンブラック MA100 (三菱化成製) 8 部、ポリプロピレンワックス (ビスコール 550P) 5 部、荷電調整剤としてセチルトリメチルアンモニウムプロマイド 2 部をヘンシェルミキサーにて混合後、2 軸混練機 (PCM-30 型、池貝鉄工製) にて 150 °C で混練させた。ついで冷却・粉碎・分級して約 7 ミクロンのトナーを得た。このトナー 3 部とキャリヤ 97 部とを混合して現像剤とし、+ チャージトナーを用いる市販の高速複写機を改造して、画像を書きかせて実施例 1 と同様にして評価し結果を表-1 に示す。

#### 【0031】実施例 8

製造例 1 で得られたビニル樹脂を製造例 7 で得られたビニル樹脂に、さらに PD6300, 10 部を 6.3 部に替えた他は実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0032】実施例 9

製造例 1 で得られたビニル樹脂を製造例 8 で得られたビニル樹脂に、さらに PD6300, 10 部を 20 部に替えた他は実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0033】比較例 1

製造例 1 で得られたビニル樹脂を用い、グリシジル化合物を用いない他は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0034】比較例 2

製造例 1 で得られたビニル樹脂を製造例 4 で得られたビニル樹脂に替えた他は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1

に示す。

#### 【0035】比較例 3

製造例 1 で得られたビニル樹脂を製造例 6 で得られたビニル樹脂に替えた他は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0036】比較例 4

製造例 1 で得られたビニル樹脂を製造例 7 で得られたビニル樹脂に替えた他は実施例 1 と全く同様にしてトナーを得、実施例 1 と全く同様にして画像評価し結果を表-1 に示す。

#### 【0037】[トナーの評価方法]

1) 定着性; 市販の高速複写機 (72 枚/分のコピースピード) でコピーし、このコピーしたベタ黒部分と白地の間を消しゴム (トンボ鉛筆社製プラスチック消しゴム "MONO") により、一定の力で 100 回往復させ、ベタ黒部分の黒度をインキ濃度計で測定し、トナーの残存比率を濃度比で表した。

2) オフセット性; 市販の高速複写機 (72 枚/分のコピースピード) で連続 100 枚コピーし、その時のオフセット発生の有無を調べた。

【0038】○; オフセット全く発生せず

△; オフセット僅かに発生

×; オフセット完全に発生

3) ブロッキング性; 重合トナーを温度 50°C、相対湿度 50% の環境下に 1 週間放置した後の粉体の凝集の程度を目視にて以下の様に測定した。

◎; 全く凝集していない

○; わずかに凝集しているが、容器を軽く振るとほぐれる

△; 容器を良く振ってもほぐれない凝集物がある

×; 完全に団塊化している

4) 画質再現性; 市販の高速複写機 (72 枚/分のコピースピード) でトナーを定着、定着前後のトナーの大きさを顕微鏡で観察し、定着後の大きさが元のトナーの何倍に成了ったかを求める。

5) 粉碎性; トナー製造時、2 軸混練後冷却したものを一部採取して粉碎し、16 メッシュアンダー 28 メッシュオンの粒度に揃えてジェットミルにて粉碎した。コールターカウンターにて粒度分布を測定、5 ~ 10  $\mu$  の粒度の割合を求める。

◎; 85% 以上

○; 70 ~ 85%

△; 50 ~ 70%

×; 50% 以下

6) 耐久性

市販の高速複写機 (72 枚/分のコピースピード) で 50,000 枚連続複写テストを実施、パターンをコピーし再現性をチェック、連続テスト前後で画質の違いをチェックした。

○; 前後で殆ど差がないもの

△; 連続テスト後IDが大きくダウンしたもの

×; カブリが発生し、画質が大きく乱れた。

【0039】

【表1】

測定項目	実施例1		実施例2		実施例3		実施例4		実施例5		実施例6		実施例7		実施例8		実施例9		実施例10		比較例1		比較例2		比較例3		比較例4		比較例5		比較例6						
	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値	測定番号	測定値					
組成	スチレン	87	←	←	85	87	←	←	91.5	74	87	←	93.4	55	←	←	99.4	55	←	←	99.4	25	←	←	←	←	←	←	←	←	←	←					
COOH 含有量 %	アクリル酸-ブチル メタアクリル酸-ブチル メタアクリル酸	9	—	—	30	9	—	—	6	18	9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—					
重合温度 (℃)	T <sub>g</sub>	190	180	220	190	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—					
分子量	T <sub>g</sub> (℃)	65	67	55	65	—	—	—	—	64	66	65	—	76	65	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—					
分子量 (KHN/g/t)	26	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—					
分子量 Mn	5,200	8,200	2,700	5,400	5,200	—	—	—	—	5,300	5,400	5,200	—	22,000	5,000	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
ジ リ ン ジ エ ボ キ シ 酸 Mw	Mw500	—	—	—	—	—	—	—	—	PD6300	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—				
分子量 Mw Mw/Mn	0.19	—	—	—	—	—	—	—	0.10	0.19	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—				
分子量 Mw/Mn 平均	8,000	—	—	—	—	—	—	—	8,000	8,000	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—				
T <sub>g</sub> (℃)	52	—	—	—	—	—	—	—	56	52	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
ビニル極端/ 环状化合物比	86/10	—	—	—	—	—	—	—	86/5	86/10	86/10	86/6.3	86/20	86/0	86/10	86/1.5	86/50	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
同上 COOH/EDTA モル比 ( / )	2/1	—	—	—	—	—	—	—	4/1	4/1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
定着性 (%)	89	87	92	90	90	—	—	—	—	92	93	92	—	92	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
オフセット性 (℃)	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○				
耐久性	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○				

【0040】表1

【発明の効果】表1に示した如く、本発明の方法により、高速機によく対応出来、しかも高解像度で且つ画質

に優れており、粉碎性も良好で、実用上優れた性能を有している。